ADVANCED CHEMISTRY

INORGANIC CHEMISTRY H.W. - WINTER - WEEK 7

From Chapter 5

(2) Lewis structures O_2 $|\overline{O}=\overline{O}|$

O_2^{2-} $[|\overline{\underline{O}}-\overline{\underline{O}}|]^{2-}$

Cannot draw a Lewis structure for O_2^- since it has an odd number of electrons.

According to the above two structures O_2 has a stronger bond (double bond) than O_2^{2-} (single bond). Bond length is O_2 is less than that of O_2^{2-}.

The three M.O. diagrams for O_2, O_2^- and O_2^{2-} are on the next 3 pages.

For O_2: Bond order $= \frac{1}{2}(10-6) = 2$

For O_2^-: Bond order $= \frac{1}{2}(10-7) = 1.5$

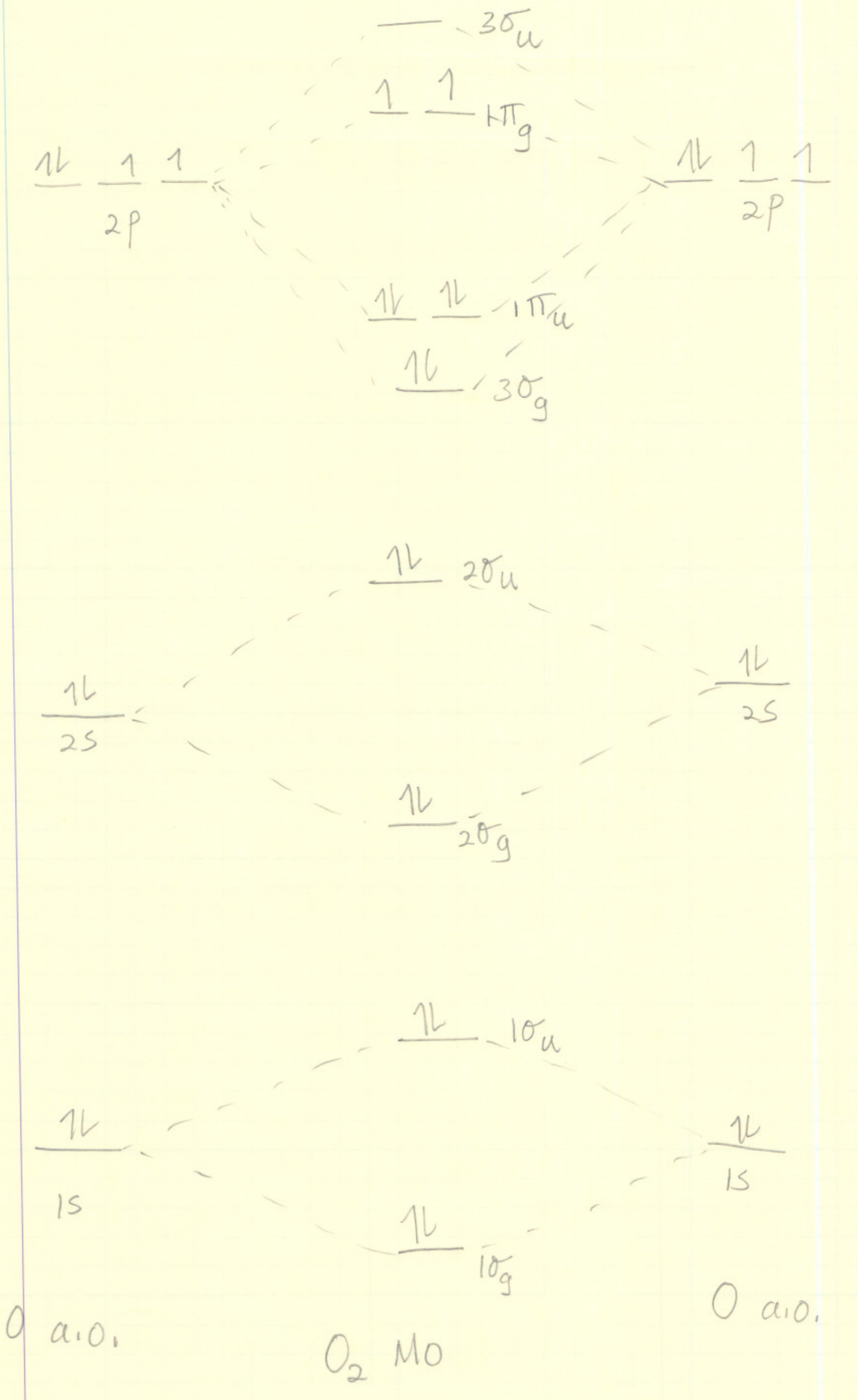
For O_2^{2-}: Bond order $= \frac{1}{2}(10-8) = 1$

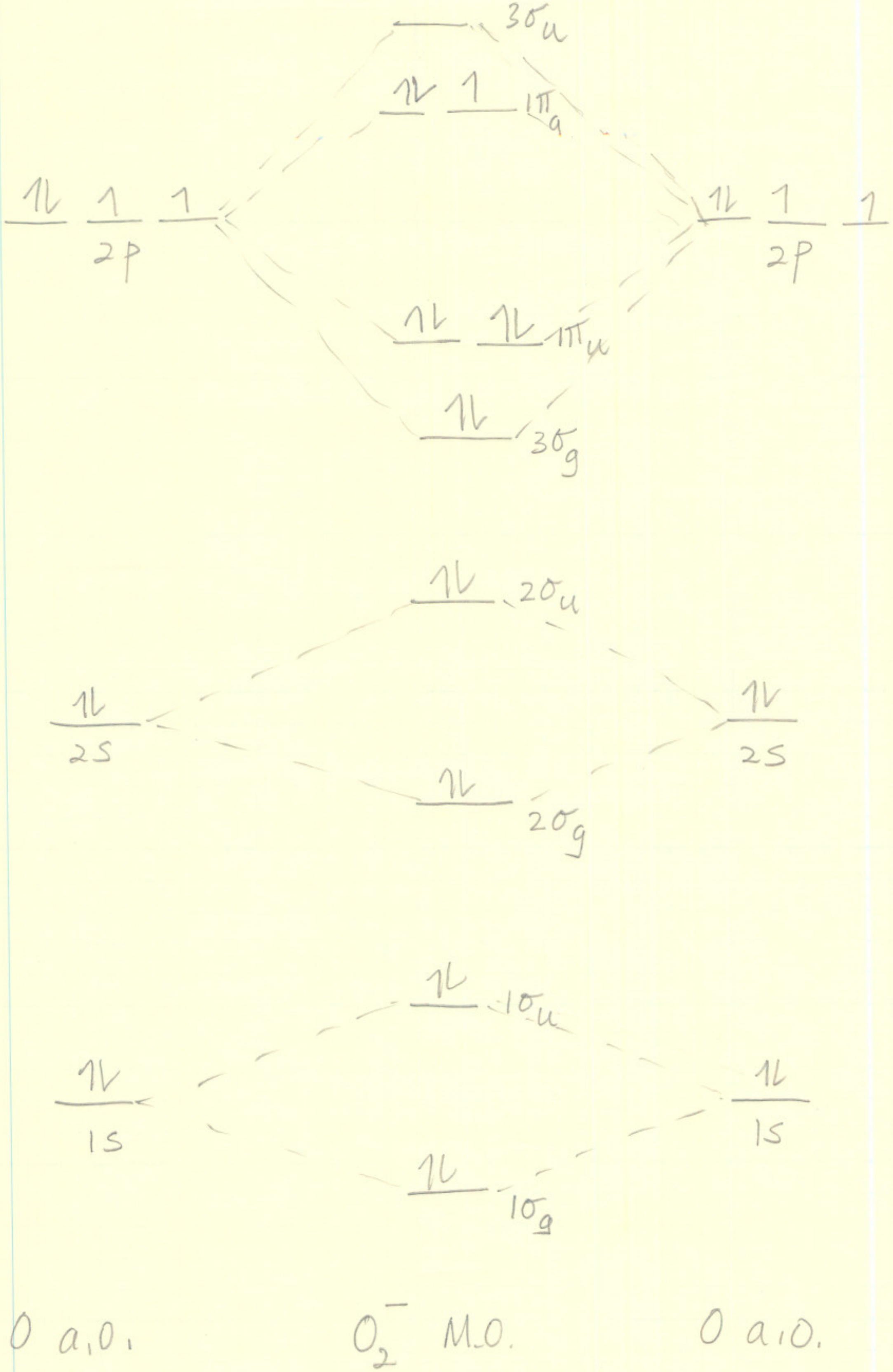
$O_2 > O_2^- > O_2^{2-}$

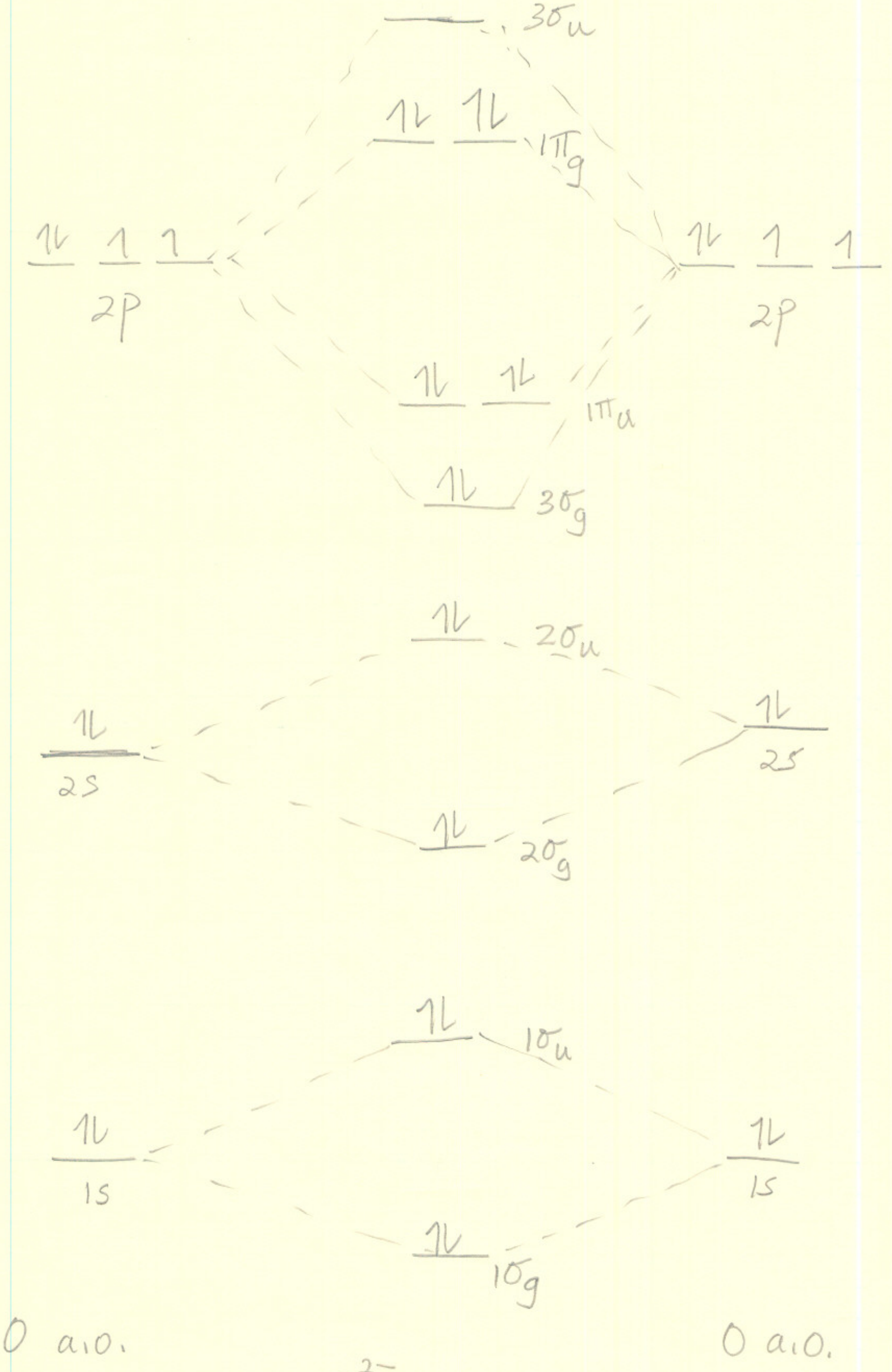
⟶ bond order decreases

⟶ bond strength decreases

⟶ bond length increases

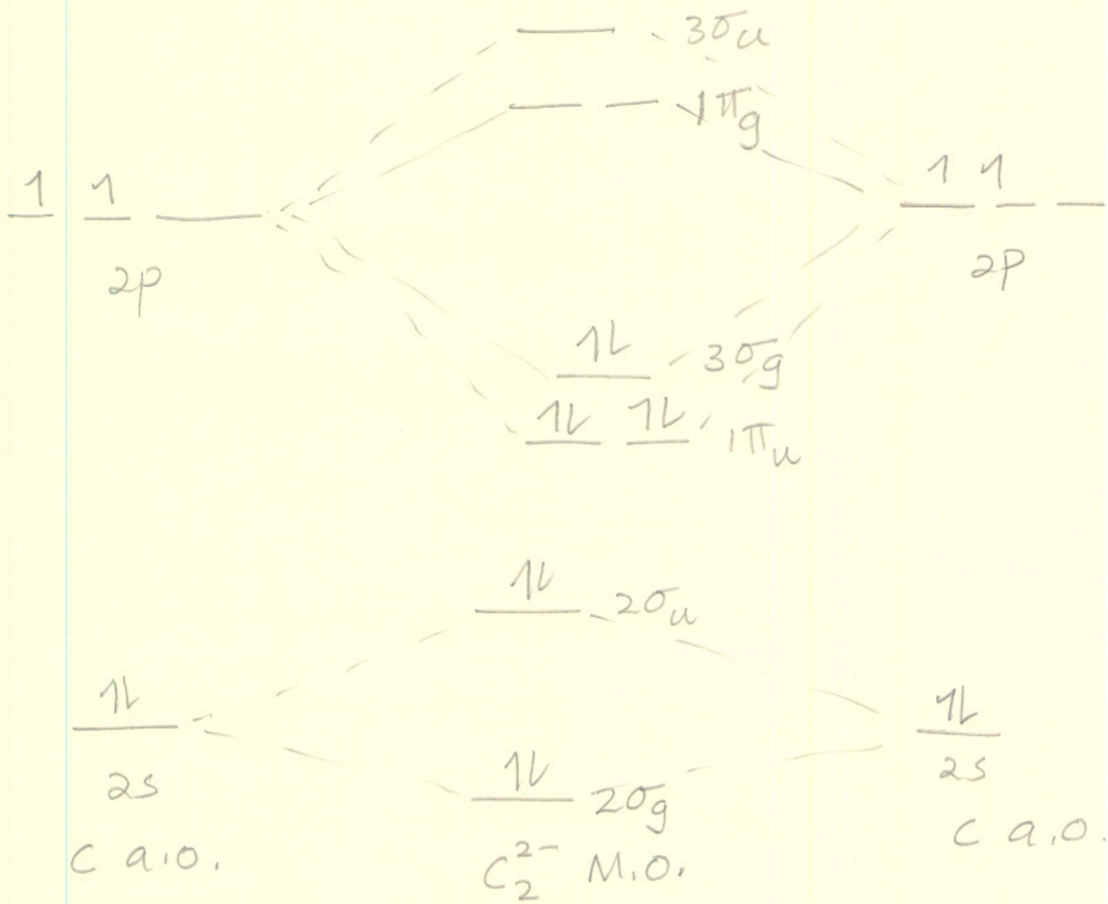

3σu
1πg
2p
2p
1πu
3σg
2σu
2s
2s
2σg
1σu
1s
1s
1σg
O a.o.
O a.o.
O2 MO


3σu
1πg
2p
2p
1πu
3σg
2σu
2s
2s
2σg
1σu
1s
1s
1σg
O a.o.
O2− M.O.
O a.o.

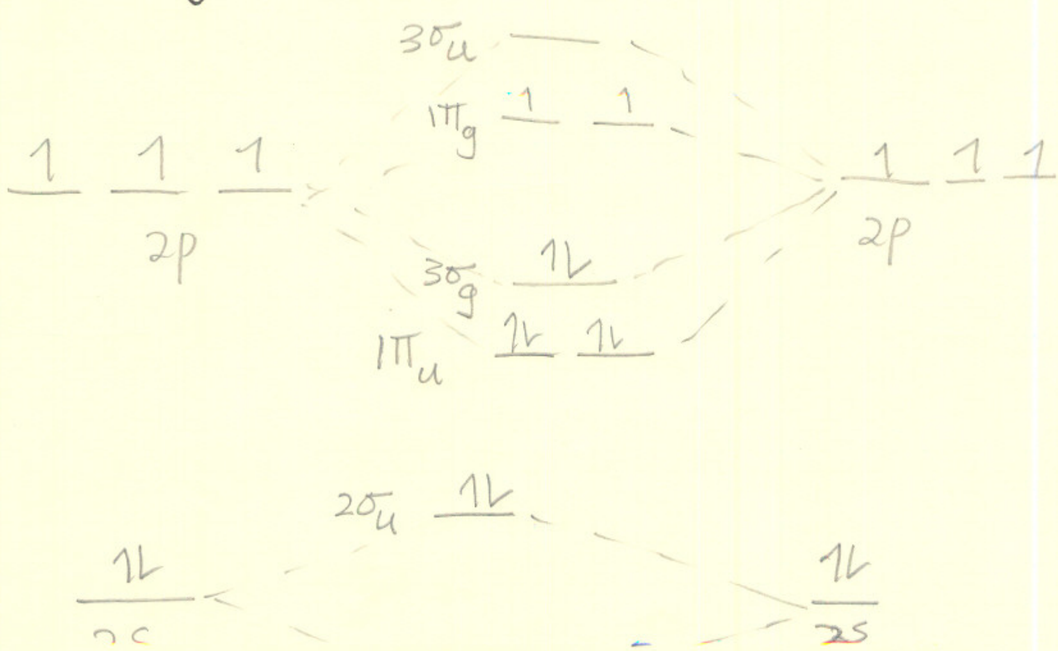


O_2^{2-} M.O.

③ MO diagram for C_2^{2-} (ignoring core electrons)



MO diagram for N_2^{2-} (ignoring core electrons)

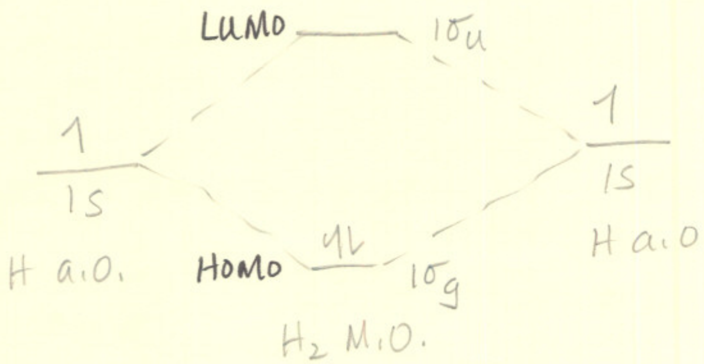


	bond order	bond length	# unpaired $\bar{e}$
C_2^{2-}	$\frac{1}{2}(8-2) = 3$	triple bond	$\underline{\underline{0}}$
O_2^{2-}	$\frac{1}{2}(10-8) = 1$	single bond	$\underline{\underline{0}}$
N_2^{2-}	$\frac{1}{2}(8-4) = 2$	double bond	$\underline{\underline{2}}$

The bond length in N_2^- is between that of C_2^{2-} and O_2^{2-}.

From the worksheet

MO diagram of H_2



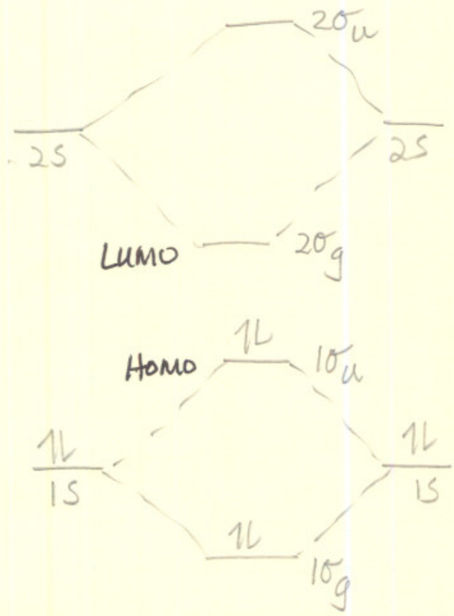
bond order $= \frac{1}{2}(2-0) = \underline{\underline{1}}$

stable

diamagnetic

$\bar{e}$ config: $1\sigma_g^2$

MO diagram for He_2



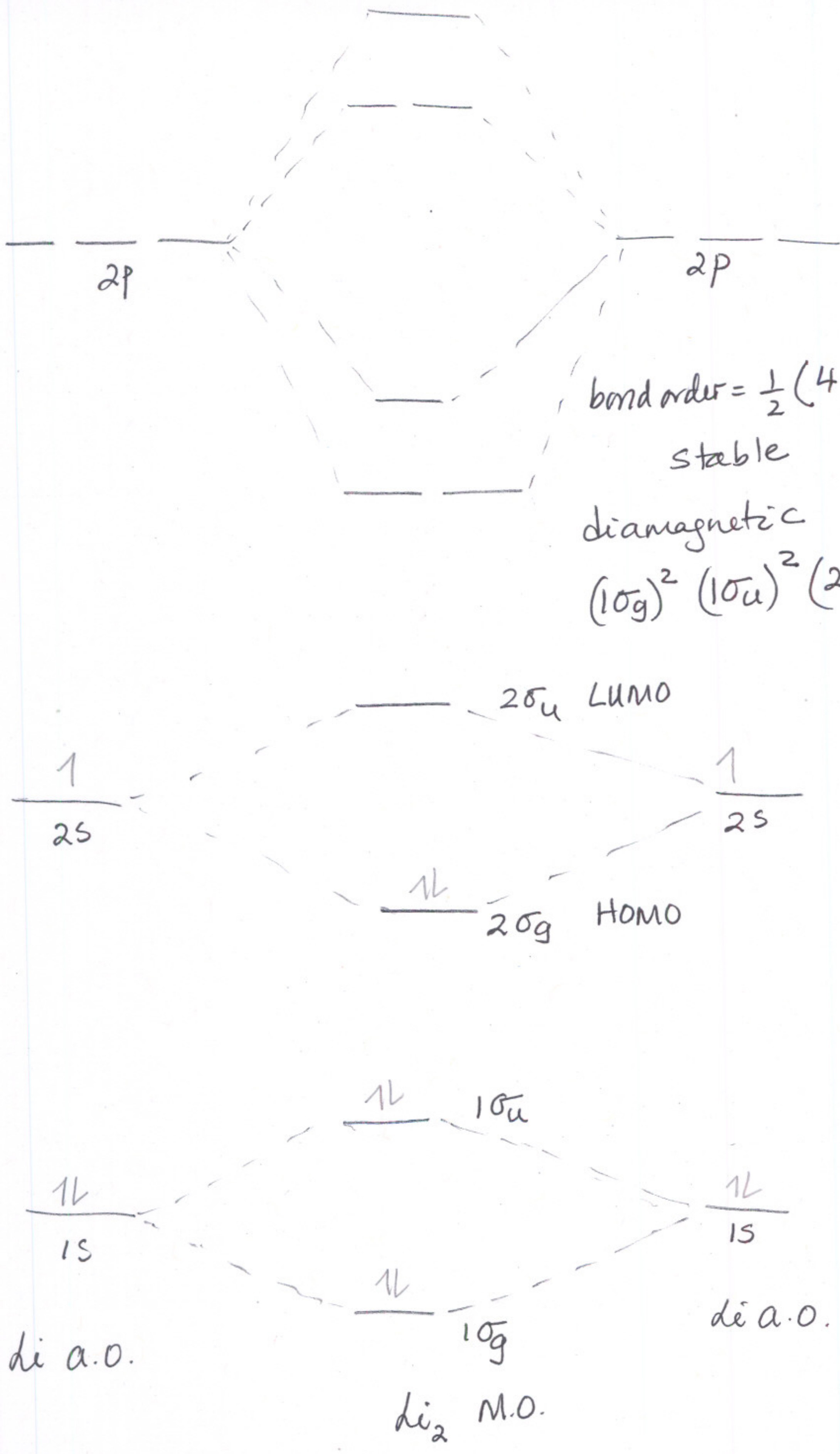
bond order $= \frac{1}{2}(2-2) = \underline{0}$

unstable

diamagnetic

$(1\sigma_g)^2 (1\sigma_u)^2$

MO diagram of Li_2



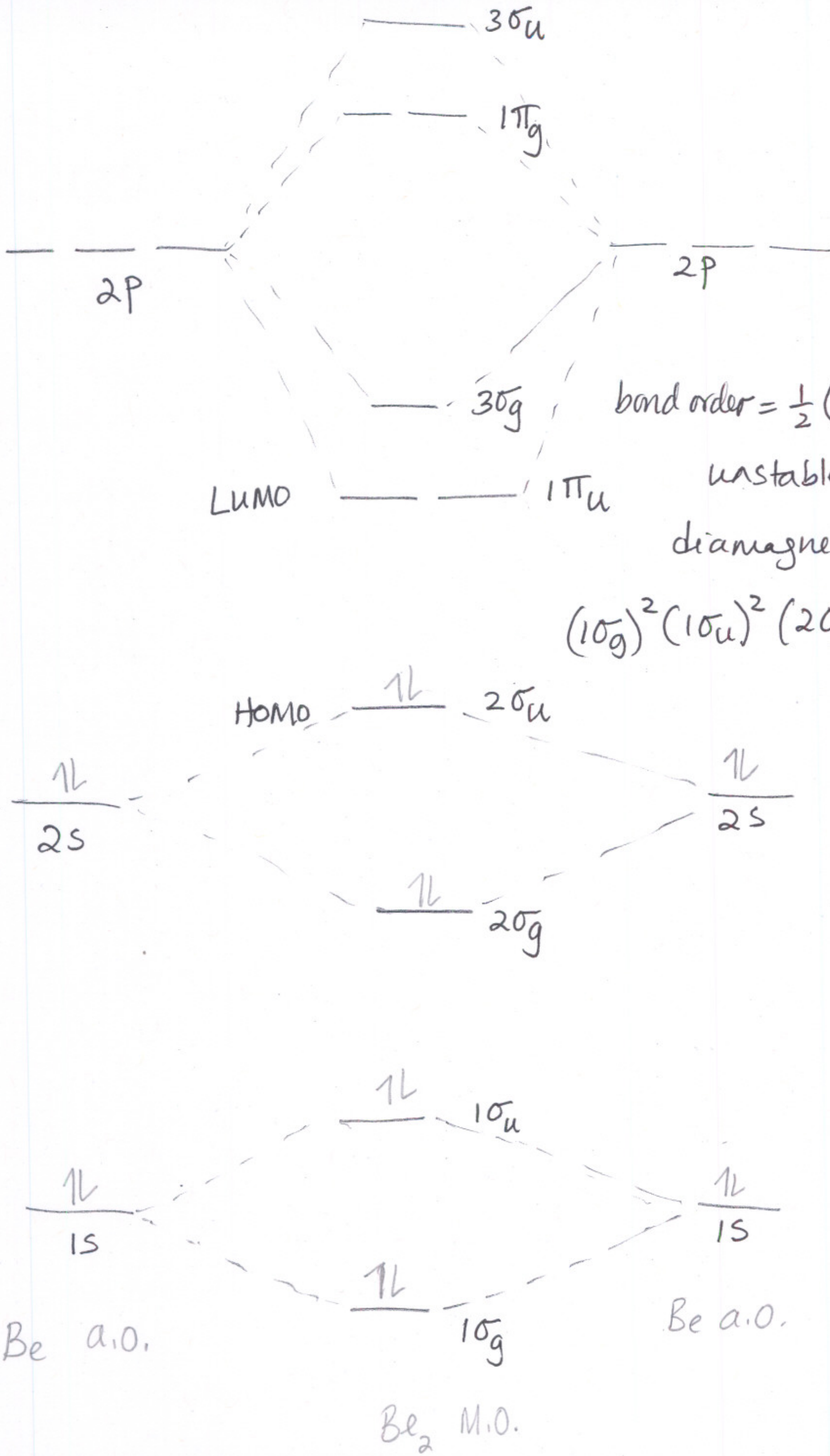
bond order = $\frac{1}{2}(4-2) = 1$

stable

diamagnetic

$(1\sigma_g)^2 (1\sigma_u)^2 (2\sigma_g)^2$

MO diagram for Be_2



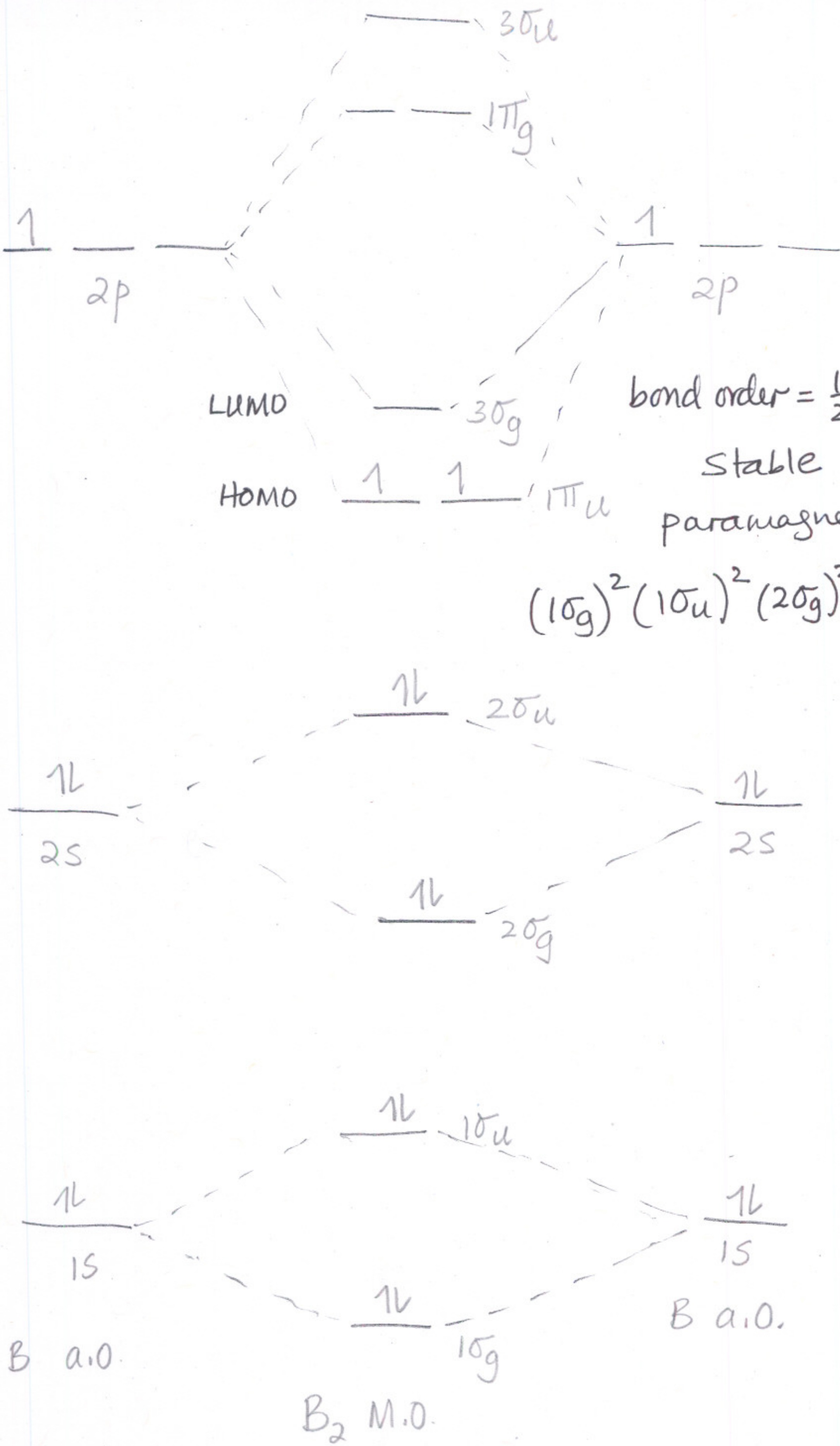
bond order $= \frac{1}{2}(4-4) = 0$

unstable (no bond)

diamagnetic

$(1\sigma_g)^2(1\sigma_u)^2(2\sigma_g)^2(2\sigma_u)^2$

MO diagram for B_2



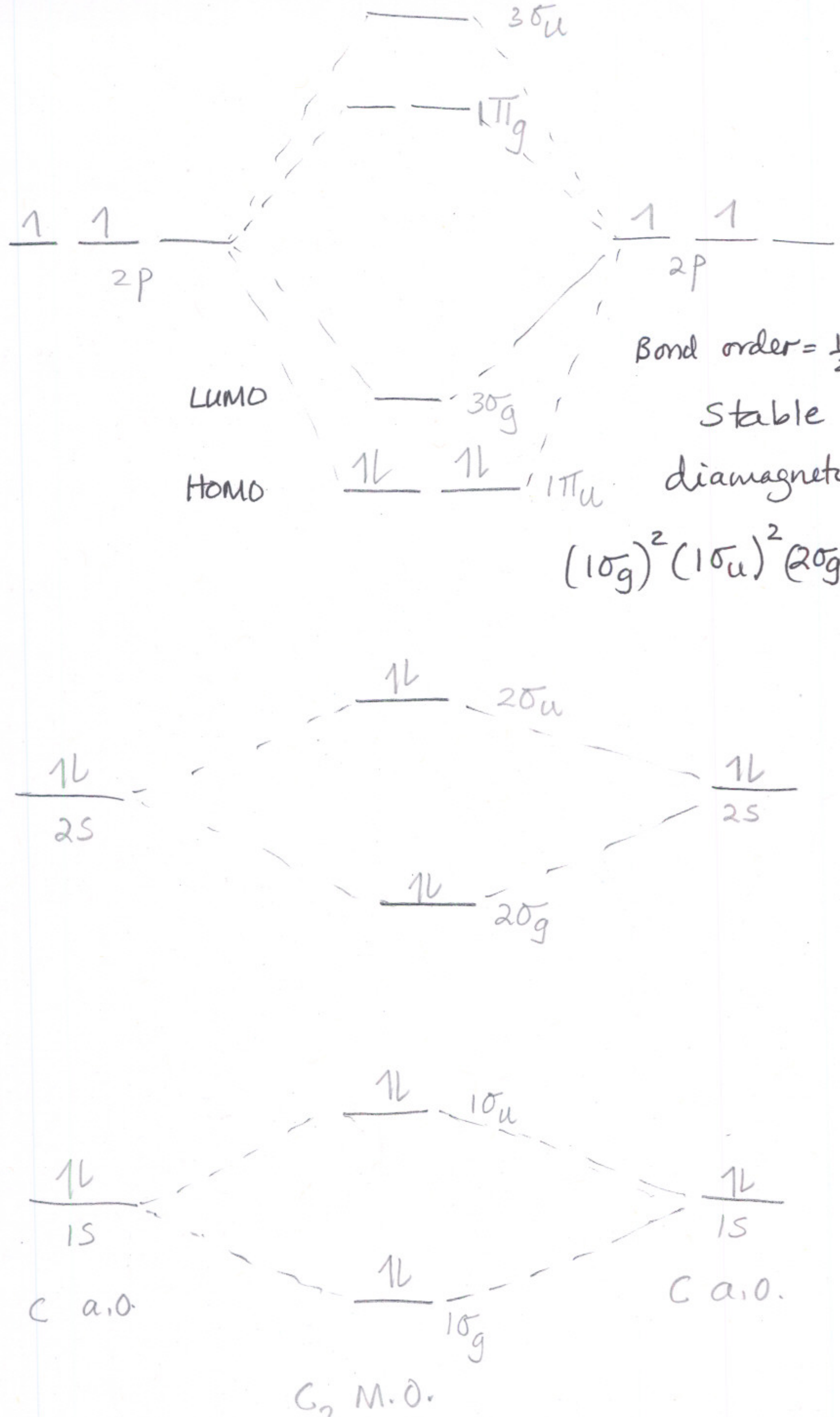
bond order $= \frac{1}{2}(6-4) = 1$

stable

paramagnetic

$(1\sigma_g)^2(1\sigma_u)^2(2\sigma_g)^2(2\sigma_u)^2(1\pi_u)^2$

M.O. Diagram for C_2



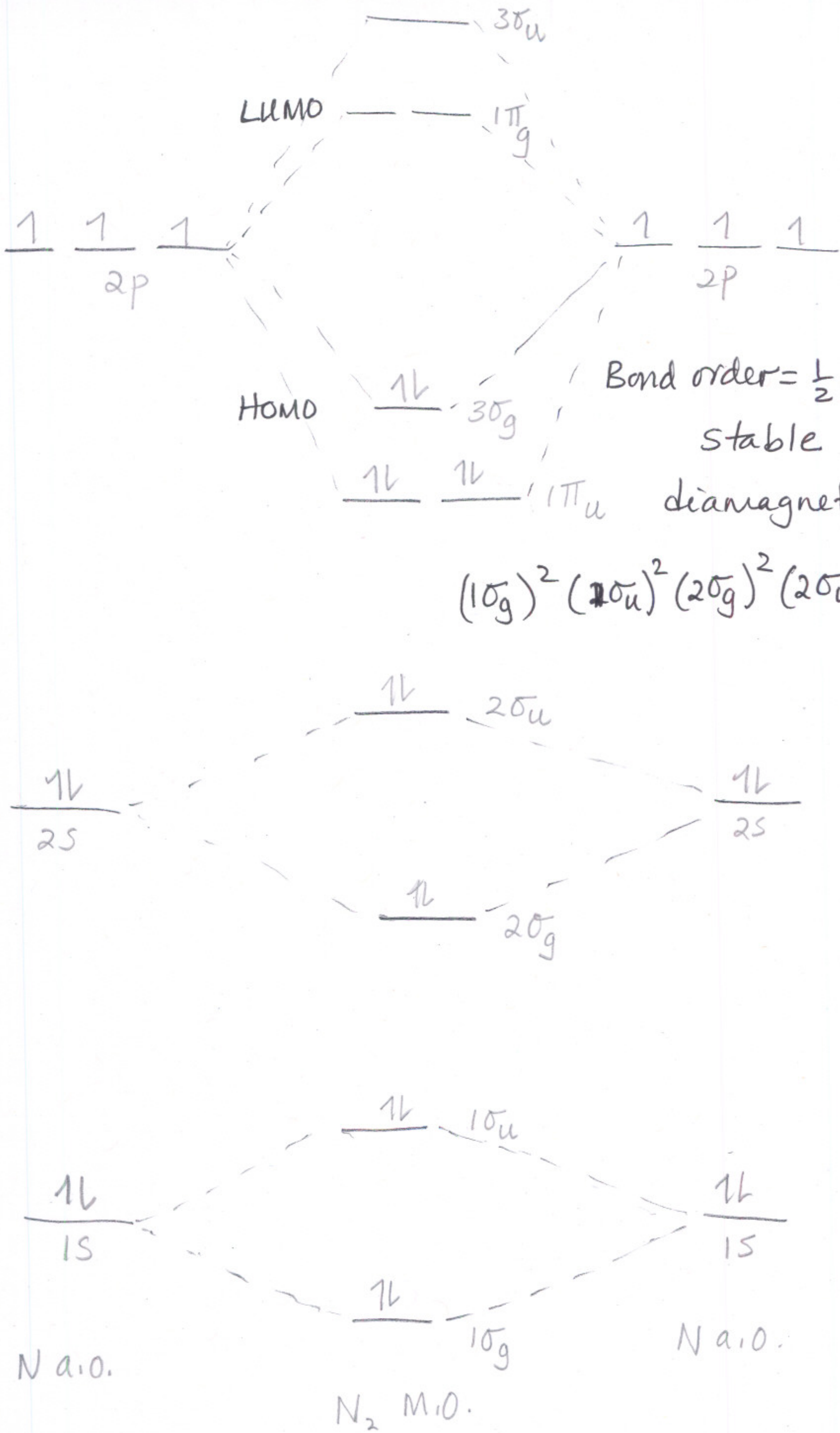
Bond order $= \frac{1}{2}(8-4) = 2$

Stable

diamagnetic

$(1\sigma_g)^2(1\sigma_u)^2(2\sigma_g)^2(2\sigma_u)^2(1\pi_u)^4$

MO diagram for N_2



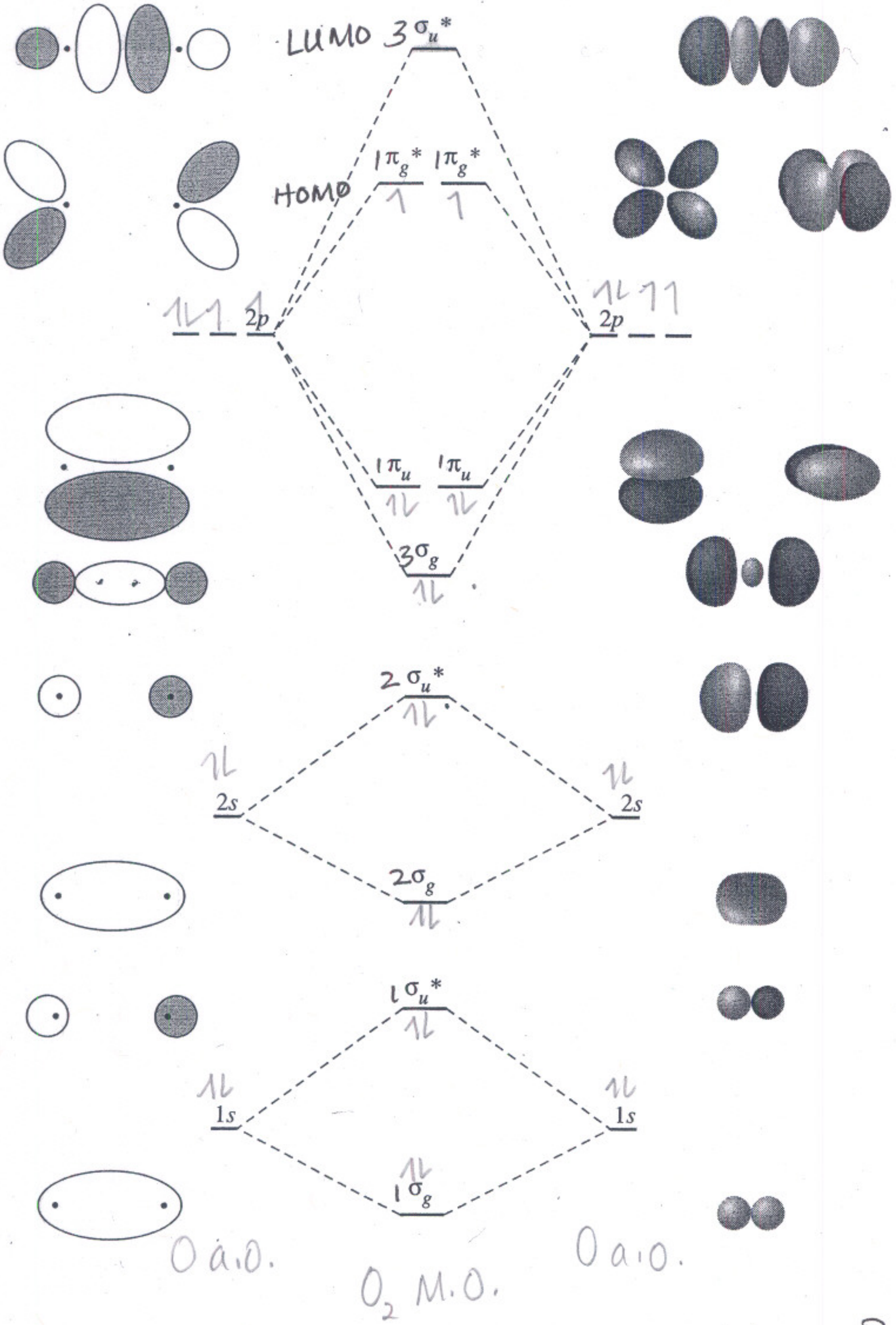
Bond order $= \frac{1}{2}(10-4) = 3$

stable

diamagnetic

$(1\sigma_g)^2(1\sigma_u)^2(2\sigma_g)^2(2\sigma_u)^2(1\pi_u)^4(3\sigma_g)^2$

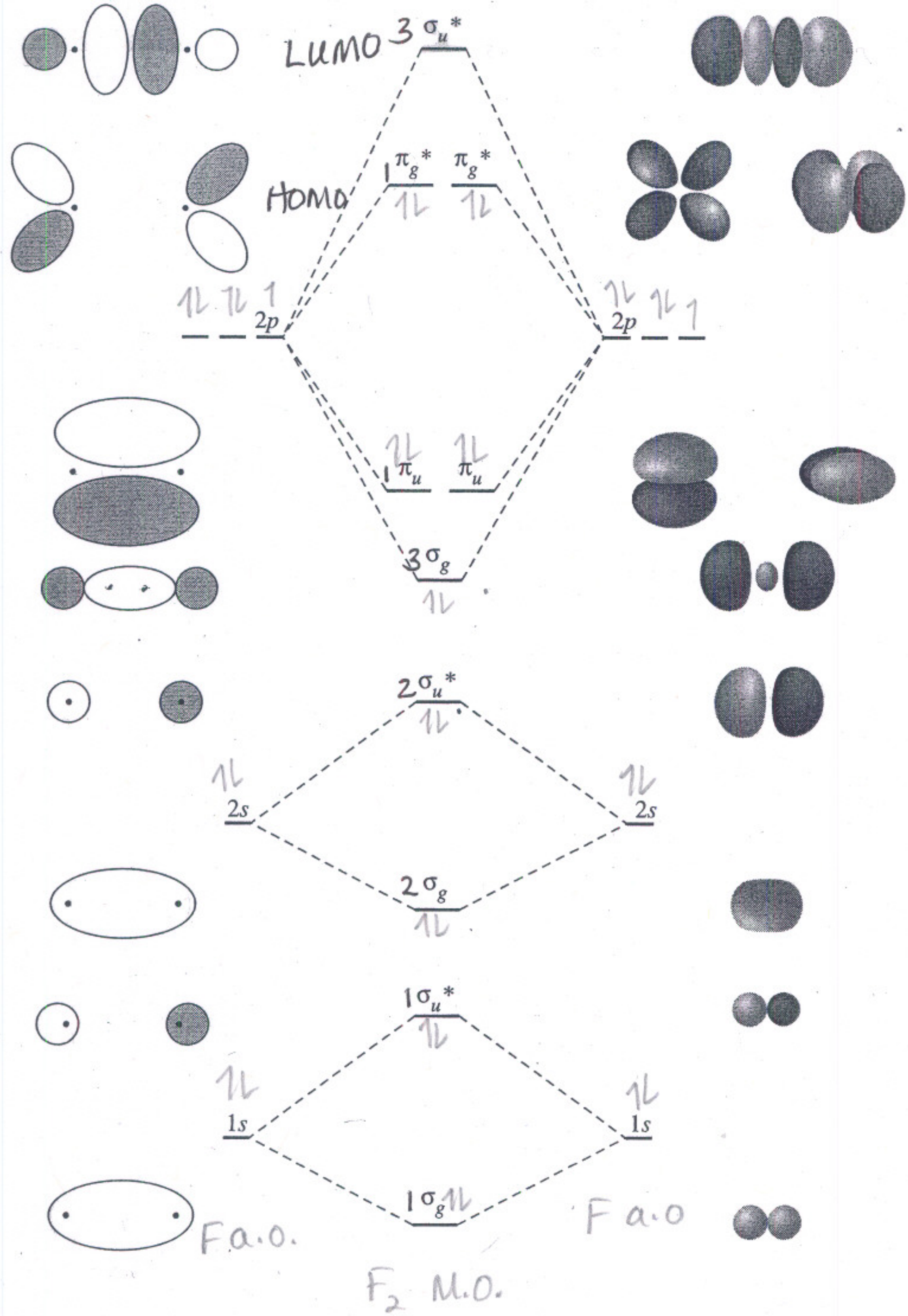
MO Diagram for O_2



Bond order $= \frac{1}{2}(10 - 6) = 2$ stable Paramagnetic

$(1\sigma_g)^2 (1\sigma_u)^2 (2\sigma_g)^2 (2\sigma_u)^2 (3\sigma_g)^2 (1\pi_u)^4 (1\pi_g)^2$

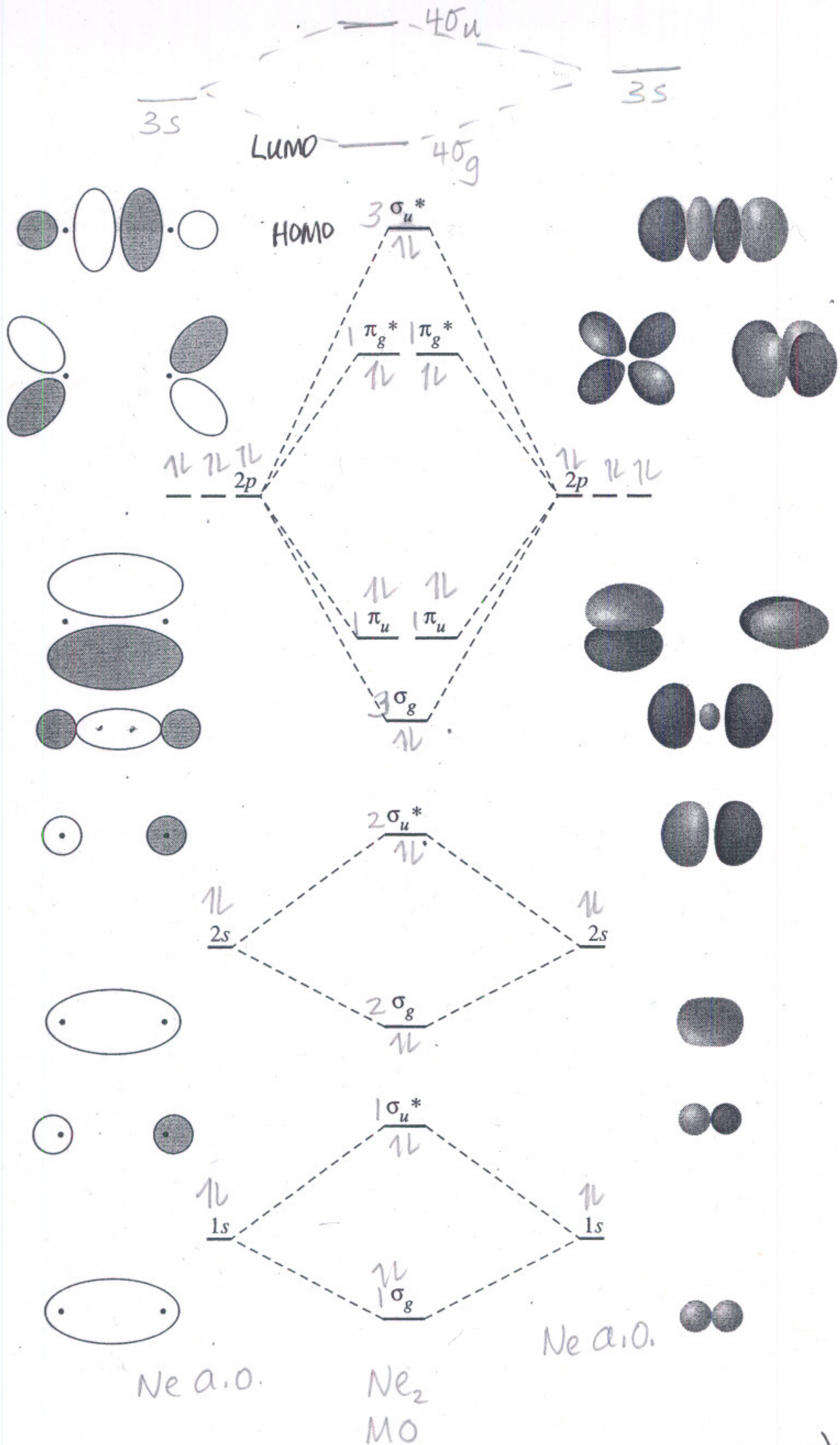
MO diagram for F_2



Bond order $= \frac{1}{2}(10 - 8) = 1$ diamagnetic   stable

$(1\sigma_g)^2 (1\sigma_u)^2 (2\sigma_g)^2 (2\sigma_u)^2 (3\sigma_g)^2 (1\pi_u)^4 (1\pi_g)^4$

MO diagram for Ne_2



Bond order $= \frac{1}{2}(10-10) = 0$ unstable (no bond) diamagnetic

$(1\sigma_g)^2 (1\sigma_u)^2 (2\sigma_g)^2 (2\sigma_u)^2 (3\sigma_g)^2 (1\pi_u)^4 (1\pi_g)^4 (3\sigma_u)^2$

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(4) The first excited state of O_2 has the electron config.

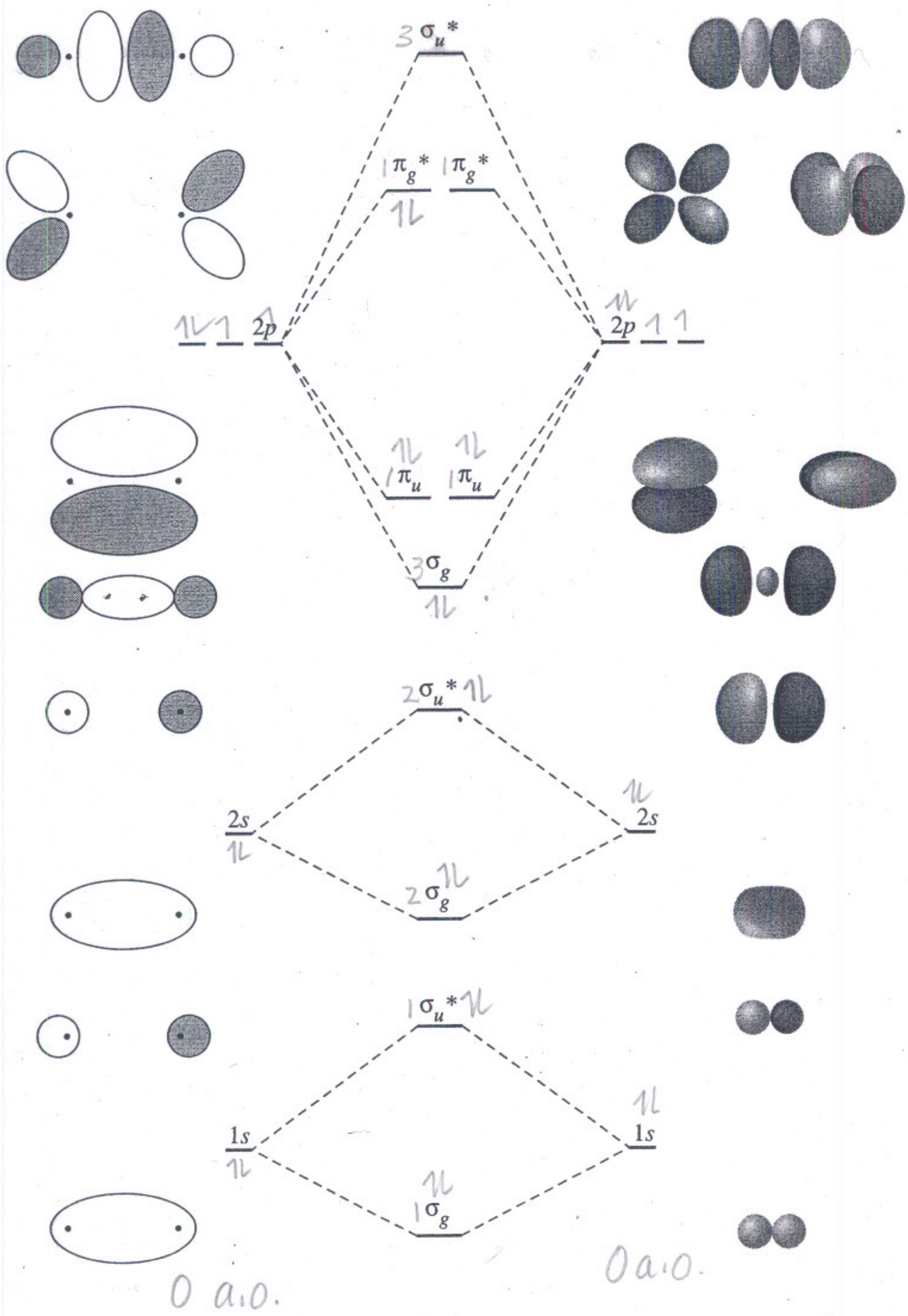
$KK (\sigma_{2s})^2 (\sigma^*_{2s})^2 (\sigma_{2p_z})^2 (\pi_{2p_x})^2 (\pi_{2p_y})^2 (\pi^*_{2p_x})^2 (\pi^*_{2p_y})^0$

and this is a <u>singlet</u> state ⇒ spin multiplicity = 1

$2S + 1 = 1$

$\Rightarrow S = 0$

KK means $(\sigma_{1s})^2 (\sigma^*_{1s})^2$



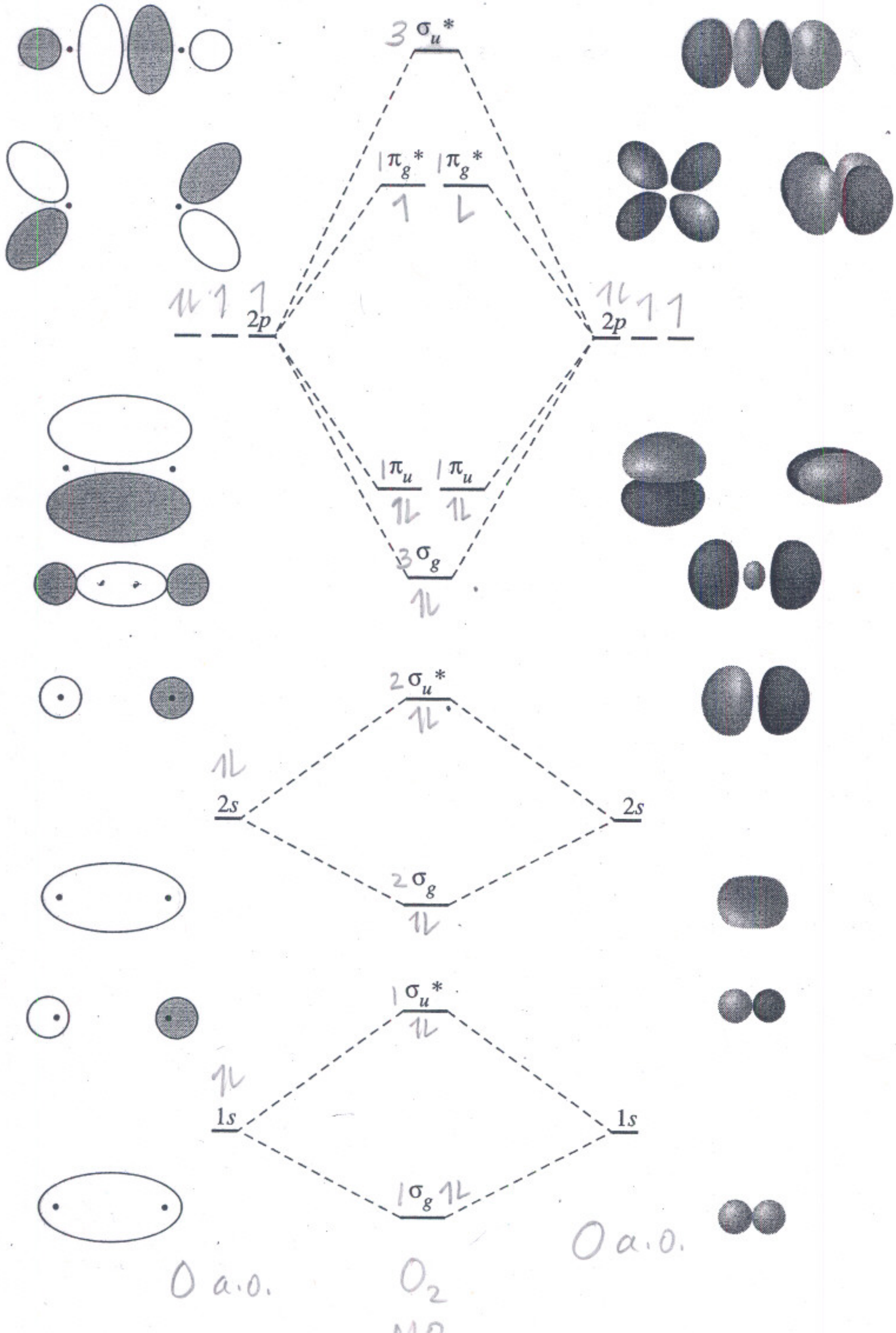
16 The second excited state of O_2 has the $\bar{e}$ config.

$KK\,(\sigma_{2s})^2(\sigma_{2s}^*)^2(\sigma_{2p_z})^2(\pi_{2p_x})^2(\pi_{2p_y})^2\,(\pi_{2p_x}^*)^1(\pi_{2p_y}^*)^1$

This is a <u>singlet</u> state ⇒ spin multiplicity = 1

$2S+1=1$

$S=0$



(4) ~~The first excited~~

If we were to draw a ladder type energy diagram for the ground state and the first two excited states of O_2, it will be as follows.